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High pressure effects on the photoluminescence intensity of sexithiophene single crystals

M.A. Loi[a,*], G. Bongiovanni[a], A. Mura[a], Q. Cai[b], C. Martin[b], H.R. Chandrasekhar[b], M. Chandrasekhar[b], W. Graupner[c], F. Garnier[d]

[a]*Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Università di Cagliari, I-09042 Monserrato (CA), Italy*
[b]*Department of Physics and Astronomy, University of Missouri, Columbia, MO 65211, USA*
[c]*Department of Physics, Virginia Tech, Blacksburg, VA-24060, USA*
[d]*Laboratoires des Materiaux Moléculaires (CNRS), Thiais, France*

Abstract

We report on the influence of interchain interactions on the light emission properties of a sexithiophene single crystal. The strength of the intermolecular interactions is controlled by applying hydrostatic pressure. The combined use of both steady-state and time-resolved photoluminescence techniques permits to show that the pressure-induced quenching of the photoluminescence is caused by a reduction of the radiative recombination rate.

Keywords: Oligothiophenes; High pressure; Photoluminescence; Time-resolved fast spectroscopy

1. Introduction

In the last years, sexithiophene has attracted a large interest for its physical properties, such as the high carrier mobility [1,2] and the stimulated emission [3]. This oligomer has been successfully used to build thin film field effect transistors with characteristics comparable to those of amorphous silicon based ones [4,5]. Furthermore, sexithiophene is at present one of the model compounds most widely used to understand the basic aspects of electronic structure and optical properties of its parent polymer. The physical properties of polymers are often masked by the structural and the chemical disorder, [6] in particular, photoluminescence has been shown to be highly dominated by defects [7]. Oligothiophene single crystals are thus particularly attractive for the low percentage of structural defects in comparison with polycrystalline thin films.

Isolated conjugated molecules are low dimensional systems. However, interchain interactions have been shown to dramatically alter the electronic and optical properties of isolated chains [8,9]. A very important quantity like the photoluminescence efficiency in conjugated materials varies over a wide range and is strongly affected by the environment of the molecules [10]. Generally, the efficiency is high if there are weak intermolecular interactions with other identical conjugated molecules (solutions, inert matrices) [11,12] and low when these intermolecular interactions become important (solid-state) [13]. Therefore, interchain interactions are of basic importance for the optical properties of conjugated molecules. In this work, the application of high pressure was selected as a way to modulate interchain interactions by reducing the intermolecular separation.

Most of the previous investigations on the photoluminescence (PL) quenching induced by pressure have been performed by using steady-state techniques or by employing spectroscopies with low time resolution. The PL quenching results from a critical balance between radiative and non-radiative recombination channels. The latter can be due to the confluence of different processes like the generation of both intrachain and interchain excitations, defects, etc., the relative strength of which characterizes the class of the semiconductor under investigation. For this reason, there is no a single time scale characterizing the non-radiative decay, but several characteristic lifetimes ranging from subpicosecond to several nanoseconds. In this paper, we investigate the influence of pressure on the electronic and emission properties of a sexithiophene single crystal, by using steady-state and time-resolved photoluminescence spectroscopy with resolution down to a few hundred femtoseconds. The combined use of both techniques at low and high temperature allows us to understood the role played by

* Corresponding author.
E-mail address: loima@alfis.dsf.unica.it (M.A. Loi).

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extrinsic (defects) and intrinsic processes on the drop of luminescence intensity induced by interchain interaction.

2. Experimental

Sexithiophene (T6) single crystals were grown by sublimation under argon atmosphere [6]. Pressure studies were conducted in a Merrill–Bassett-type diamond anvil cell (DAC) with cryogenically loaded argon or ethanol–methanol mixture as pressure medium and ruby luminescence as pressure calibrant. The cw photoluminescence spectra conducted on the sample under pressure were taken by a high-resolution double grating SPEX 1401 monochromator, the detector was a GaAs photomultiplier tube. The 488.0 nm (2.54 eV) line of an Ar-ion laser was used to excite the sample. To perform low temperature measurements the DAC was adjusted on the cold finger of a closed-cycle cryostat.

The time-resolved PL was studied both by using femtosecond photoluminescence up-conversion spectroscopy technique with a resolution of 200 fs [14], and a Hamamatsu optical sampling oscilloscope with time resolution of 20 ps. The emission was excited by the second harmonic of a mode locked Ti:Sapphire with typical pulse width of 150 fs tuned at 810 nm.

3. Results and discussion

Fig. 1 shows the evolution with temperature of the PL spectra of the T6 single crystal. The spectrum at low temperature shows a fine structure typical of the single crystal [7,15–17]. The sharp components are superimposed on a broad background that has been attributed to excitons trapped at crystal defects (aggregates) [7]. All the fine features of the emission have been explained [7,15–17] in terms of vibronic progressions [18] of the lowest exciton level a_u. This level is weakly allowed in the crystal and thus most of the intensity of the vibronic replicas is acquired via Herzberg–Teller vibronic coupling with higher excitonic levels [7]. Following the assignments given in [7] and [15–17], the narrow peaks at 2.093 and 1.913 eV form a vibronic progression with the ground state totally symmetric mode of 181 meV, built on the luminescence origin (O) at 2.273 eV. The vibronic progression with peaks at 2.146 and 1.966 eV is built on the luminescence false origin (O′) at 2.234 eV, which promotes a ground state totally symmetric mode of 38 meV. With increasing temperature, the fine structure broadens and the contribution to the PL spectrum from aggregates decreases. At 300 K, this thermal de-trapping gives rise to a purely excitonic recombination to the phonon band of the ground electronic state involving the internal CC stretching mode of 181 meV [19]. A similar temperature behavior has been recently reported for a thin film of T6 [20].

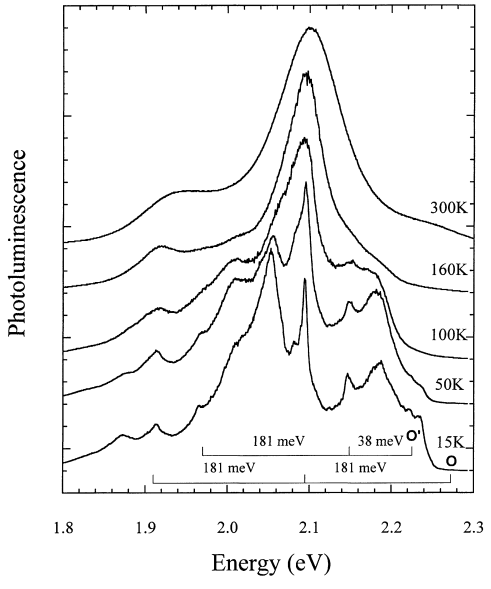

Fig. 1. Evolution of the photoluminescence spectra of the T6 single crystal with the temperature. All the spectra are normalized to the maximum of the intensity, and are displaced vertically for clarity. Following [7] and [15–17], O is the origin of the photoluminescence and O′ is the false origin.

Fig. 2 shows the PL spectra of the T6 single crystal at 300 K for different pressures. The spectra show a considerable shift to the red on going from ambient pressure to 55 kbar. The shift rate, 4.1 meV kbar^{-1}, is comparable with that found in similar materials [21,22]. The origin of the shift is related to the increasing intermolecular interaction with the applied pressure [23]. In this paper, we do not directly address this issue for a detailed discussion on the topics, we refer to the existing literature [24,25]. The shape of the main peak in Fig. 2 does not change, and the less intense band at lower energy, to which several emissions probably take part, shows only a slight broadening. From this general line-shape analysis, we conclude that free exciton emission persists and dominates even at the highest pressures.

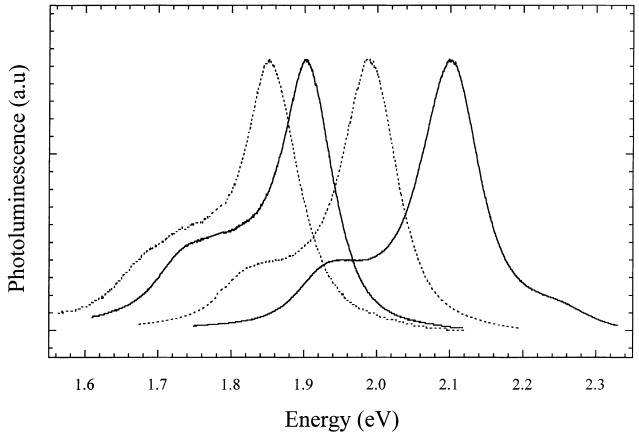

Fig. 2. Photoluminescence spectra (exc. 2.54 eV) of T6 single crystal at different pressure (300 K), from high to low energies, ambient pressure, 19, 41 and 55 kbar. All the spectra are normalized to the maximum of the intensity.

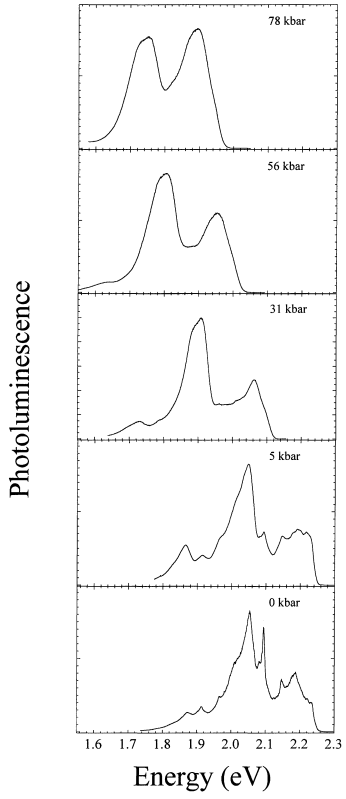

Fig. 3. Photoluminescence spectra (exc. 2.54 eV) of T6 single crystal at different pressures and 15 K. All spectra are normalized to the maximum of the intensity.

At low temperature, free and trapped exciton emissions coexist. When pressure is applied (Fig. 3), the shape of the PL spectra drastically changes, and the free exciton features quickly disappear. At pressures above 5 kbar, emission from aggregates dominates. The relative intensities of the different bands change, but they shift rigidly with pressure as shown in Fig. 4. The shift of all the luminescence features at low and high temperatures is similar, indicating that radiative traps are related to the same excitonic band [19]. The

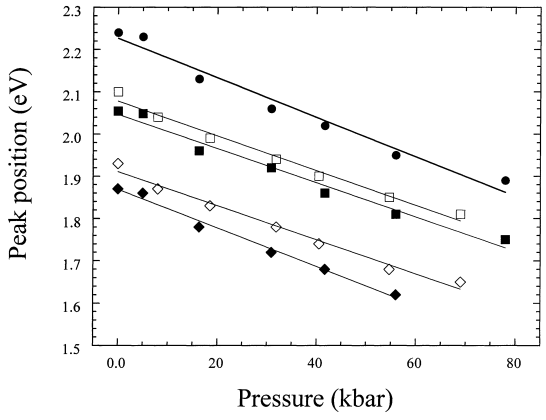

Fig. 4. Evolution of the peak position energy with the pressure at 300 and 15 K, empty and full symbols, respectively.

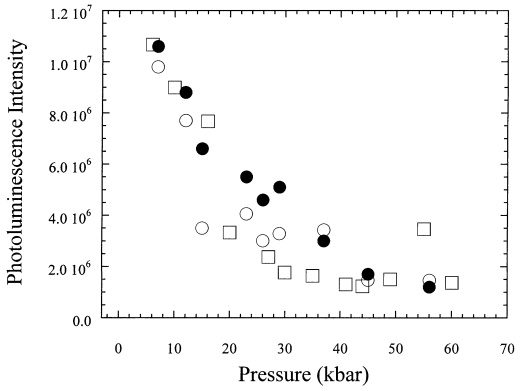

Fig. 5. Intensity of the PL at 300 K from the time-resolved decays (exc. 3.06 eV, 3 mW) full circles, cw PL spectra (exc. 3.06 eV, 3 mW) empty circles and time-resolved decays (exc. 2.33 eV, 3 mW) empty squares. All the values are scaled to coincide at ambient pressure.

decrease of the intermolecular distance (high pressure) enhances the exciton transfer rate between chains. The intermolecular coupling can be estimated from the excitonic bandwidth. From absorption measurements, the latter has been evaluated to be 322 meV at ambient pressure [15–17], and 612 meV at 70 kbar [26]. The resulting faster transfer rate (roughly a factor two at 70 kbar) augments the capture cross-section by radiative defects, and thus gives rise to the purely aggregate emission observed in the cw-experimental PL spectra under pressure at low temperature (Fig. 3).

The decrease of the cw PL intensity as a function of the pressure is reported in Fig. 5. From ambient to 60 kbar, the emission intensity, excited by photons with energy of 3.06 eV, reduces by a factor ten. The PL intensity and shape are restored on going from 60 kbar to ambient pressure.

Different physical processes have been suggested to explain the quenching of the photoluminescence under high pressure [22]. The mechanisms proposed are due to extrinsic properties related to the presence (or formation) of non-radiative centers, or to intrinsic properties of the material, like the formation of excited states having a weak or no radiative coupling to the ground state, e.g. charge transfer (CTE) excitons, self-trapped excitons [23]. The formation of some of these species, namely self-trapped excitons, can be ruled out by inspection of the PL shape, as they should lead to much broader emission bands [27].

Fig. 6 shows that the PL decays recorded by means of a streak tube with 20 ps time resolution. The temporal behavior is non-exponential. At short delays, the decay rate slightly increases with pressure. At long times, however, the slope of the decay becomes longer (0.9 ns) and independent of pressure.

The radiative and non-radiative life-times of non-interacting T6 molecules in solution are 4 and 1.0 ns, respectively [28]. τ_{nr} is due to inter-system crossing to the triplet manifold and to internal conversion [22,29]. In T6 crystal, the radiative life-time should be even much longer, as the transition to the lowest exciton level is dipole forbidden.

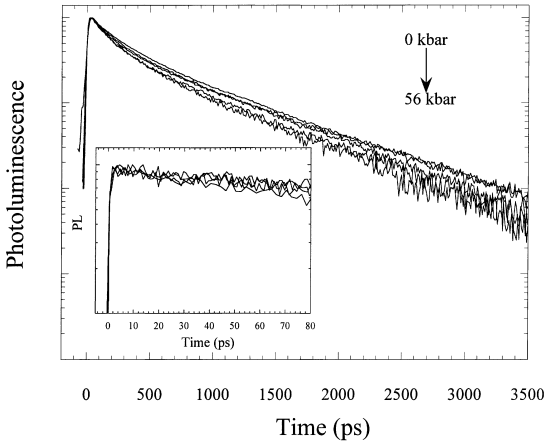

Fig. 6. Time-resolved decays (exc. 3.06) of T6 single crystal from ambient pressure to 56 kbar. The insert shows the decay of the up-conversion signal from ambient pressure to 37 kbar. All the decays are normalized to the maximum of the intensity.

Thus, the decay rate of the PL signal, is only determined by the non-radiative recombination rate. The non-exponential behavior of the PL intensity, and in particular the initial faster decay, has to be ascribed to exciton diffusion towards quenching centers [30,31]. This is confirmed by two experimental observations: (i) a variation of about 20% of the fast decay is found when probing different regions of the sample; (ii) the initial decay rate becomes faster when increasing the number of quenching centers by means of a prolonged UV irradiation in air.

According to the diffusion model, at long times the probability that an exciton is trapped at a non-radiative center becomes negligible, and the PL goes as $\exp(-t/\tau)$, where t is the intrinsic non-radiative lifetime due to the decay of thermalized excitons into long-lived secondary photoexcitations like triplet excitons (TE), charge-transfer excitons, and uncorrelated polaron pairs (P^+P^-), or due to non-radiative internal conversion. In the present experiment, $t = 0.9$ ns perfectly matches the non-radiative decay of the single T6 molecule at all pressures. This result implies that (i) the long-time generation rate of inter-chain species, namely CTE and P^+P^-, is negligible with respect to the total non-radiative cross-section. A very low dissociation time of excitons is in very good agreement with the recent experimental measurements of the photogeneration quantum efficiency of η charge excitations in T6 single crystal, which gives a value of $\eta = 10^{-4}-10^{-5}$ [1,2]. (ii) Intersystem crossing and internal conversion rates from the lowest excited state in the non-interacting molecule and in the crystal are the same. That remains still true when a very high pressure is applied to the T6 crystal. On the basis of this latter point (ii), we infer that the intramolecular Frenkel character of excitons [32], which in conclusion determines the size of τ_{nr}, is retained when intermolecular interactions are switched on in the crystal. That the electron-hole pair forming the lowest singlet excitons in T6 crystals resides on the same molecule fairly agrees with recent electron energy loss measurements [32]. Our experiments further show that the Frenkel nature of the lowest exciton is preserved even at pressures as high as 60 kbar.

Finally, the slight increase of the initial PL decay with pressure derives from the enhanced exciton transfer rate between chains. Assuming an equal density of photogenerated excitons at $t = 0$, the integrated area of the different PL transients shown in Fig. 6 provides an evaluation of the reduction of the quantum efficiency due to the faster decay. The reduction estimated in this way is only 20% on going from 0 to 60 kbar. The increased exciton transfer rate with pressure can not thus explain the high quenching of the PL. This result is confirmed by the fact that the behavior of the emission intensity at $t \sim 0$, i.e. before slow diffusion processes take place, and the cw PL intensity as a function of pressure are similar (see Fig. 5).

There exist several experimental evidences that CTE, P^+P^-, and TE can be efficiently generated from singlet exciton during the thermalization time [33]. The generation efficiency strongly depends on the excess energy of the laser photons with respect to the bottom of the excitonic band. As thermalization occurs in several hundreds of femtoseconds [18], we have investigated the contribution of these processes to the overall non-radiative recombination rate by using up-conversion time-resolved PL techniques. The experimental curves at different pressures are reported in the inset of Fig. 6. These data show that the decay in the early time of the PL transients does not become faster increasing pressure. A complementary confirmation of the time-resolved measurements has been obtained by changing the excitation energy. In Fig. 5, we have reported the emission intensity at $t \sim 0$ excited by 2.33 eV photons (well below the transition energy 2.78 to the CTE [1,2,15–17]), as a function of the applied pressure. Although the excess energy has been drastically reduced from 787 down to 57 meV, we observe a similar quenching of the PL. These experimental measurements provide therefore strong evidence that the generation of neutral and charged excitations is not responsible for the PL quenching under pressure on T6 crystal.

The reduction of the quantum emission efficiency has therefore to be related to a decrease of the exciton radiative decay rate, which, as already stated, barely influences the size of the exciton density and PL lifetime. Assuming an emission decay via Herzberg–Teller coupling, the radiative decay rate is proportional to the square of the derivative of the electronic transition moment with respect to the internal phonon mode Q, responsible for the coupling between the lowest exciton band $|\mathrm{ex}_1\rangle$ and higher energy levels $|\mathrm{ex}_j\rangle$, i.e. $1/\tau_r \propto |\{\Sigma_j \langle \mathrm{g}|\mu|\mathrm{ex}_j\rangle\langle \mathrm{ex}_j|\partial U/\partial Q|\mathrm{ex}_1\rangle/(E_1 - E_j)\}_0|$ [3,34], where $|\mathrm{g}\rangle$ is the ground state, μ is the dipole-moment, $E_1 - E_j$ is the energy difference between the level $|\mathrm{ex}_1\rangle$ and $|\mathrm{ex}_j\rangle$, and the second factor in the expression represents the vibronic coupling between excitonic levels. From this equation, emission can be seen as an indirect transition to the ground state which involves intermediary states $|\mathrm{ex}_j\rangle$. Two

possible changes in the exciton wavefunctions, energies, and vibronic couplings can be effective in reducing $1/\tau_r$. If the dominant intermediate state is the first dipole-allowed excitonic level, the increased value of $E_1 - E_2$ (a factor two) [26] with pressure should reduce the PL intensity by a factor four. The other possibility concerns the fact that increasing pressure, the intermolecular electronic coupling enters in the strong coupling regime, namely the ratio between the excitonic bandwidth and internal phonon energy exceeds by far 1. In the present experiment, at 70 kbar this ratio is $\sim 612/181 = 3.4 \gg 1$. In this regime, the vibronic coupling is expected to decrease considerably, as intermolecular transfer is so rapid relative to a vibrational period that the molecules are expected to remain fixed near their ground state equilibrium structure throughout [34].

4. Conclusions

We have studied the influence of intermolecular interaction on the light emission efficiency in a single T6 crystal. Due to the high quality of the sample, emission at room temperature mainly arises from decay of bulk excitons. Steady-state and time-resolved studies show that excitons retain their intramolecular character even though the applied pressure considerably enhances the intermolecular electronic interaction. In the range of pressure between 0 and 70 kbar, a strong quenching of the photoluminescence is observed. Time-resolved measurements show that such a reduction of the quantum yield is related to a decrease of the radiative decay rate and not to an increase of generation rate of neutral and charged interchain excitations.

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